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A Polymorph Lost and Found: The High-Temperature Crystal Structure of Pentacene**

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Pentacene has become an important organic-semiconductor material, with potential applications in thin-film transistors[1] and single crystals.[2–4] The triclinic structure of crystalline pentacene was first reported in 1961.[5,6] However, this particular structure has not been reproduced in subsequent crystal-growth experiments. Various structure determinations on single crystals grown in different ways have consistently revealed different triclinic structures[7–9] (e.g. polymorph). Such discrepancies might be taken to suggest that the apparent polymorphism in pentacene requires the presence of impurities during crystallization.

Polymorphism in pentacene, on the other hand, has been observed in as-prepared powders[10] and thin-film growth experiments. For thin films, four different crystalline phases have been identified by using X-ray diffraction.[9,11] In all of these phases, pentacene molecules align their long axis approximately perpendicular to the film surface, and are thought to adopt a herringbone-type arrangement in the resulting two-dimensional layers.[9,12,13] Several different *d*-spacings perpendicular to the thin-film surface have been observed, with values of 14.1, 14.5, 15.0, and 15.5 Å,[11,13] sometimes used to label the different polymorphs. The relative concentration of these phases appears to be strongly dependent upon the deposition conditions. The different values are thought to be caused by varying tilt angles of the molecules from the surface normal, with the shortest *d*-spacing of 14.1 Å, consistent with the recent room-temperature single-crystal structure of pentacene,[7–9,13] and the 14.5 Å *d*-spacing consistent with the initial structure reported by Campbell.[5,6] None of the other thin-film polymorphs of pentacene have been observed in crystals grown by physical vapor-phase transport[8,9] or from solution.[7,9] Single crystals of pentacene grown by physical vapor-phase transport, although appearing well crystallized to visual inspection, often show large mosaic spreads. Because of the large and anisotropic thermal-expansion coefficient in pentacene, with one direction even showing negative thermal expansion,[9,14] large stress/strain fields are expected upon cooling, producing a high density of small-angle grain boundaries. Electronic-transport measurements on such crystals are influenced by trap formation, presumably at grain boundaries, and other defects produced during the growth process. Further minimization of such defects is needed to access the intrinsic electronic properties of single-crystalline pentacene.[14,15]

Two polymorphic forms with different volume fractions are often observed in powders. X-ray powder diffraction and Raman scattering allow identification of the two polymorphic forms,[16] and pressure experiments have revealed that the 14.5 Å polymorph irreversibly transforms into the 14.1 Å polymorph at elevated pressures.[10,17,18] Energy-minimization using quasi-Monte-Carlo sampling have been employed to study the stability of polymorphs of pentacene: the two observed phases (14.1 Å and 14.5 Å) represent the deepest energy minima,[19] that is, the most stable forms of pentacene. Despite interest in the use of pentacene as an organic-semiconductor material, and the continuing efforts to characterize the various crystal forms, doubts have remained until now about both the existence of a high-temperature polymorph of pentacene and its structure and thermal-expansion properties. We have investigated the nature of the (often incomplete) phase transformation between the two polymorphs. The information gleaned from these studies has implications on the optimization of crystal-growth procedures, both for single crystals and for thin-film devices.

Single crystals of pentacene evaluated at room temperature often show a large mosaic, extending over several tenths of a degree, although individual grains are well crystallized. This is in contrast to rubrene, for example, where an excellent mosaic structure is observed, with a mosaic spread of less than 0.02°.[20] Upon heating pentacene powders, we observed an incomplete phase transformation to a new polymorph starting at around 463 K, with the new phase showing a larger *d*-spac-

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ing of 14.5 Å. Upon cooling, this phase could be observed down to room temperature, indicating quenching of this high-temperature phase, consistent with previous observations of polymorphism in pentacene powders.[18] Our first attempts to use powder diffraction to obtain a crystal structure of the high-temperature phase were hampered by the fact that no single-phase powder pattern could be obtained, and the peak overlap between the two phases was substantial. Further experiments using single crystals heated to temperatures above 463 K eventually provided sufficient data for a single-crystal structure determination. However, the large stress/strains produced by the phase transformation often resulted in the loss of the crystal during measurements (e.g. the sample cracked and even "jumped" off the mount). Furthermore, sublimation of pentacene at even higher temperatures was substantial, hampering the data collection.

The existence of two enantiotropic polymorphs that transform at high temperature (albeit incompletely in powder form) allows us to assign the following nomenclature: pentacene-LT (stable <463 K) and pentacene-HT (stable >463 K). Alternatively, the nomenclature described by Herbstein[21], designates pentacene-LT as EI and pentacene-HT as EII.

The unit cell refined for pentacene-HT also has triclinic symmetry, $P1$, with a = 6.119(2) Å, b = 8.058(2) Å, c = 15.097(4) Å, α = 80.88(2)°, β = 77.68(2)°, and = 85.89(2)°. This unit cell is set up to facilitate the comparison between the two polymorphs. However, it can be transformed to the values given in Table 1.

The pentacene-HT unit cell is consistent with the unit cell first reported by Campbell et al.[5] The crystal structure of pentacene-HT is shown in Figure 1, with the low-temperature polymorph (pentacene-LT) superimposed to illustrate the relative molecular displacements. Individual herringbone-type layers are virtually identical and can be superimposed on each other, whereas adjacent layers are shifted in the pentacene-LT crystal system by (0.295, -0.174, 0.033) in fractional coordinates, or by (1.74 Å, -1.23 Å, 0.47 Å) in an orthogonal system with the x-axis parallel to the a-axis, and the z-axis parallel to the c*-axis. The vertical shift of 0.47 Å between the layers accounts for the increased d-spacing to 14.5 Å, whereas the tilt angles of the molecules change very little. The herringbone layer rearranges slightly, with a decrease of 0.15 Å in the a-axis, and an increase of 0.13 Å in the b-axis, as determined from powders at 503 K with a volume ratio between pentacene-LT and -HT close to 1:1. Furthermore, their respective unit-cell volumes are also very close, 715.5(6) Å^3 (LT) and 717.9(6) Å^3 (HT).

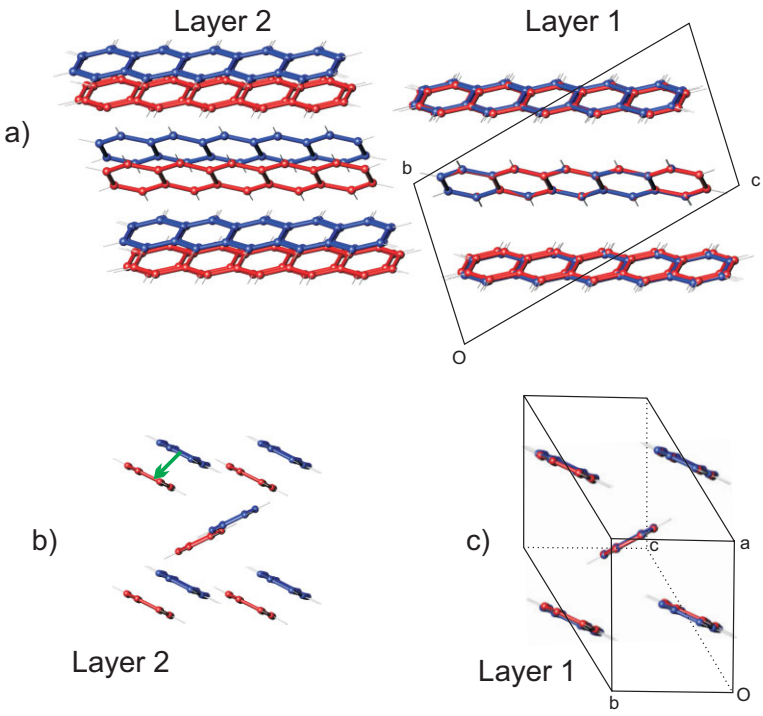

Figure 1. The crystal structure of the two pentacene polymorphs superimposed (blue: low-temperature (pentacene-LT); red: high-temperature (pentacene-HT) phase). In (a), the layered type of the herringbone structure is illustrated. Layer 1 and layer 2 (its adjacent layer) are isolated and drawn in a different orientation in (b) and (c) respectively. The arrow in (b) indicates how the layers are shifted in the two different crystal structures.

Table 1. Unit-cell parameters of pentacene-HT and -LT.

Unit-cell parameters	Pentacene-HT (478 K)	Pentacene-HT (reduced cell)[22] (478 K)	Pentacene (Campbell)[5, 6] (reduced cell)[22]	Pentacene-LT (reduced cell)[22] (293 K)
a	6.119(2) Å	6.119(2) Å	6.14(2) Å	6.265(2) Å
b	8.058(2) Å	8.058(2) Å	7.93(2) Å	7.777(2) Å
c	15.097(3) Å	14.926(3) Å	14.905(4) Å	14.536(3) Å
α	80.88(2)°	97.52(2)°	96.8(5)°	76.48(1)°
β	77.68(2)°	100.19(2)°	100.5(5)°	87.67(1)°
γ	85.89(2)°	94.11(2)°	94.1(5)°	84.71(1)°

The phase transformation is of the first order, as evidenced by the co-existence of two phases over a broad temperature range from powder diffraction (Fig. 2), the abrupt change observed in the scattering pattern in the single-crystal experiment, and the fact that both phases have the same symmetry.[23,24] In Figure 3, we show the (002) reflection of pentacene-HT versus temperature (pentacene-HT appears at 463 K). During the phase transformation the layers rearrange in different relative positions, finding another "nesting" configuration. The type and density of structural defects is expected to strongly influence the kinetics of the phase transformation, which proves to be very sluggish in powders and results in large hysteresis.[18] In powders, where the number of defects is expected to be large, pentacene-LT and -HT coexist even at room temperature (with an approximate LT/HT ratio of 20:1 at 290 K), or far above the phase-transformation temperature (LT/HT = 1:20 at 563 K), with a gradual change of

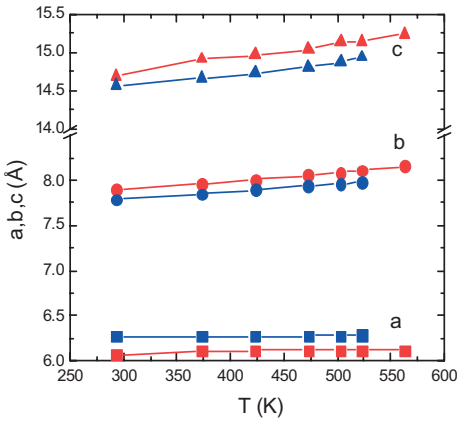

Figure 2. Temperature dependence of the unit-cell parameters of both pentacene-LT (blue) and pentacene-HT (red) obtained from powder diffraction.

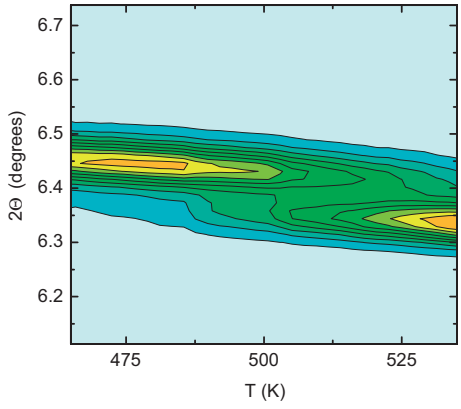

Figure 3. Powder diffraction of the pentacene-LT and -HT (002) reflection versus temperature.

the ratio of the phases with temperature in between. This phase coexistence may also be a reason for the difficulty in observing the phase transformation in differential scanning calorimetry (DSC) experiments, where data from powders showed inconclusive results. In contrast, phase transformation is well defined in single crystals, although significant undercooling is possible. The difference in behavior between single-crystal and powder samples could indicate a spread of transition temperatures over crystallites caused by defect-induced stress fields. Furthermore, the large shift between the herringbone-type layers often results in shattering of the crystal.

The relative thermal expansion tensor of pentacene-HT was determined according to the procedure outlined previously,[25] using the unit-cell data derived from powder measurements at 373 and 563 K (Fig. 2). The two large relative thermal expansion directions lie between the *b*- and *c*-axes, with values of $110(10) \times 10^{-6}$ K^{-1} and $133(13) \times 10^{-6}$ K^{-1}. Interestingly, a slight contraction of $-3(2) \times 10^{-6}$ K^{-1} unit strain is calculated for the third direction, which is approximately parallel to the *a*-axis. This negative thermal expansion is consistent with the relative negative thermal expansion observed in the pentacene-LT, which is more pronounced with a value of $-31(6) \times 10^{-6}$ K.[14]

The nature of the phase transformation is also of interest for thin-film growth. As films often have a *d*-spacing of 14.5 Å, they most likely crystallize in the pentacene-HT structure, and are thus metastable. The design of a thin-film processing technique therefore has to take into account that an incomplete phase transformation might occur at higher temperatures, leading to large stress/strain fields in the films that will induce defect formation. Furthermore, a recent powder diffraction pattern obtained from a scraped off thin film indicates another, different, unit cell, with $a = 6.485$, $b = 7.407$, and $c = 14.745$ Å; and $\alpha = 77.25°$, $\beta = 85.72°$, and $\gamma = 80.92°$,[9] which is not consistent with either pentacene-LT or -HT. Therefore, further polymorphic phases of pentacene have to be considered in the structural optimization of thin-film devices.

One might speculate about the reasons why single-crystalline pentacene-HT has not been observed since the first structure was reported. A recent attempt to reproduce the solution growth of pentacene from trichlorobenzene used a temperature of 450 K to slowly evaporate the solvent.[9] This yielded pentacene-LT, because the growth temperature was below the transformation temperature of 463 K. However, if the crystal growth described by Campbell[5] was carried out at a temperature above 463 K, but below the boiling point of trichlorobenzene of 486 K, pentacene-HT would be more stable, and fast cooling may have allowed pentacene-HT to be quenched to room temperature.

We have determined the structure of the high-temperature pentacene polymorph, pentacene-HT, which is stable above 463 K, and have shown that pentacene is an enantiotropic system. The structure of pentacene-HT is consistent with the first one reported by Campbell in 1961[5] which was not reproduced in subsequent single-crystal growth experiments. The herringbone layers are virtually identical in both polymorphs, whereas their interlayer stacking differs significantly. Both polymorphs show uniaxial negative thermal expansion, with a direction approximately along their respective *a*-axes.

In order to obtain high-quality thin films or single crystals, it is therefore necessary to minimize the temperature gradients in processing. Surface-tension effects may also play a role, because the 15.0 and 15.4 Å thin-film polymorphs are easily converted into pentacene-HT by being dipped into solvents such as ethanol, in which pentacene is not soluble.[26] Thin films often have a *d*-spacing of 14.5 Å, and hence most possibly crystallize in the metastable, pentacene-HT structure. Thin-film processing therefore has to take into account that an incomplete phase transformation might occur at higher temperatures, leading to large stress/strain fields in the films that will induce defect formation.

Experimental

Single crystals of pentacene were grown using horizontal physical vapor-phase transport as described earlier [27], or in a closed ampoule

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under vacuum. The crystals were then structurally characterized using a laboratory Oxford Diffraction Xcalibur-2 charge-coupled device (CCD) diffractometer equipped with a Cryojet temperature-control system, and using synchrotron radiation on the Swiss–Norwegian beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF)
. The beamline is equipped with an Oxford Diffraction KM6 diffractometer and a sample heater. Temperature calibration was made using a Lakeshore silicon diode. Cambridge Crystallographic Data Centre (CCDC) 619978-619982 records contain the supplementary crystallographic data for this paper; these data can be obtained free of charge from at www.ccdc.cam.ac.uk/data_request/cif.

Temperature-dependent synchrotron powder-diffraction data were also collected using a MarResearch MAR345 image-plate area detector on the SNBL. Reciprocal space maps were obtained using a custom-built triple-axis diffractometer equipped with a LiF monochromator and analyzer, with resolution of the order of 0.02°, well below the rocking curve widths in pentacene crystals.

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